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Reply to the comment on "The calculation of potential curve of $A^1\Sigma^+$ state of ^{7}LiH from experimental data" by Arvind K Sharma, Suresh Chandra and S N Behere

Reem Al-Tuwirqi* and M Rafi

Department of Physics, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

E-mail : rureem@hotmail.com

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Abstract : In the preceding comment, Sharma *et al* [*Indian J. Phys.* 75B(5) (2001)] opened questions for the potential energy curve of the $A^1\Sigma^+$ state of ^{7}LiH calculated by Al-Tuwirqi *et al* Here, this question is answered and it is maintained that the RKR curve of Al-Tuwirqi is correct

Keywords $A^1\Sigma^+$ state of ^{7}LiH, RKR potential energy curve

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The Rydberg [1]-Klein [2]-Rees [3] (RKR) method is commonly used for determining diatomic molecule potential energy curves from spectroscopically determined molecular constants. The theory for this technique is well-known and the method describes the evaluation of turning points $r_{min}(v, J = 0)$ and $r_{max}(v, J = 0)$ from the following relations :

$$r_{max} = \left(f^2 + \frac{f}{g}\right)^{1/2} + f,$$

$$r_{min} = \left(f^2 + \frac{f}{g}\right)^{1/2} - f,$$

where

$$f = \frac{1}{2}(r_{max} - r_{min}) = \left(\frac{\hbar}{4\pi c\mu}\right)^{-1/2} \int_{-1/2}^{v} \frac{dx}{G(v) - G(x)} \quad (1)$$

$$g = \frac{1}{2}\left(\frac{1}{r_{min}} - \frac{1}{r_{max}}\right) = \left(\frac{4\pi\mu c}{\hbar}\right)^{1/2} \int_{-1/2}^{v} \frac{B(x)}{G(v) - G(x)} dx . \quad (2)$$

$B(x)$ and $G(x)$ are the rotational constant and vibrational energy for level x. Spectroscopic constants used in constructing the RKR curve of an electronic state are found from the Dunham-like expressions (for details see Ref. [4]). The RKR method consists of accurately handling the integrable singularity at the upper limit in the f and g integrals given in eqs. (1) and (2). A number of computer programmes [5–7] have been used to do these integrations and give the r_{max} and r_{min} of each vibrational state.

Rafi *et al* [8–10] made absorption studies of the spectra of $A^1\Sigma^+$-$X^1\Sigma^+$ system of ^{7}LiH using a 3.4 metre Ebert spectrograph and observed the v values of the $A^1\Sigma^+$ state to 26. It is found that the vibrational intervals begin to rise with increasing v values and after attaining a maximum value of 391.50 cm^{-1} at v = 10 fall monotonically. The rotational constants B_v also follow a parallel course with increasing vibrational quantum number. Mulliken [11] attributed this peculiar behaviour to the ionic covalent avoided crossing between the ground $X^1\Sigma^+$ state and the first excited $A^1\Sigma^+$ state potential energy curves Rafi *et al* [10] worked out the Dunham coefficients of the $A^1\Sigma^+$ state of ^{7}LiH and we produce the same in Table 1. Al-Tuwirqi *et al* [12]

Table 1. Dunham coefficients Y_{ij}(cm^{-1}) for the $A^1\Sigma^+$ state of ^{7}LiH used by Al-Tuwirqi *et al* [12] taken from Table 3 of Ref. [10].

Vibrational constants		Rotational constants	
Y_{00}	7.259	Y_{01}	2.8418
Y_{10}	236.4717	Y_{11}	2.5116×10^{-2}
Y_{20}	26.8514	Y_{21}	1.8974×10^{-3}
Y_{30}	-3.3387	Y_{31}	-1.4600×10^{-3}
Y_{40}	0.3557	Y_{41}	1.4995×10^{-4}
Y_{50}	-2.96177×10^{-2}	Y_{51}	-6.3640×10^{-6}
Y_{60}	1.74293×10^{-3}	Y_{61}	9.5952×10^{-8}
Y_{70}	-7.06097×10^{-5}		
Y_{80}	1.89402×10^{-6}		
Y_{90}	-3.05187×10^{-8}		
$Y_{10,0}$	2.22147×10^{-10}		

*Corresponding Author

Table 2. RKR potential energy curve of the $A^1\Sigma^+$ state of ^{7}LiH

v	U(cm^{-1})		r_{min}(Å)			r_{max}(Å)		
	a	*b,c*	*a*	*b*	*c*	*a*	*b*	*c*
0	131 26	131 81	2 2252	2.2231	2 2516	3 0087	3 0183	2 9986
1	412 28	412 71	2 0242	2 0239	2.0566	3.2831	3 2959	3 3021
2	725 25	725 48	1 9080	1.9079	1 9517	3.4685	3 4789	3.5029
3	1060 94	1061 31	1 8244	1 8235	1 8798	3 6192	3.6268	3 6668
4	1413 74	1414.22	1 7589	1 7570	1 8263	3 7514	3 7568	3 8121
5	1779 57	1780 01	1 7050	1 7023	1 7851	3 8724	3 8766	3 9470
6	2155 19	2155 47	1 6589	1 6562	1 7530	3 9864	3 9900	4 0755
7	2537 91	2538 04	1 6189	1 6167	1 7279	4 0960	4 0994	4 2003
8	2925 47	2925 49	1 5839	1 5821	1 7083	4 2029	4.2062	4 3229
9	3315 89	3315 87	1.5528	1.5513	1 6932	4 3082	4.3116	4 4446
10	3707 44	3707 37	1 5249	1 5235	1 6817	4 4130	4 4165	4 5663
11	4098 53	4098 36	1 4994	1 4981	1 6734	4 5180	4 5214	4 6889
12	4487 70	4487 31	1 4758	1 4745	1 6679	4.6239	4 6271	4 8130
13	4873 61	4872 85	1 4541	1 4525	1 6649	4 7314	4 7342	4 9394
14	5254 97	5253 67	1 4342	1 4319	1 6645	4 8410	4 8433	5 0690
15	5630 47	5628 53	1 4162	1 4126	1.6669	4 9538	4 9552	5 2029
16		5996 20		1 3947	1.6725		5 0709	5 3423
17		6355 41		1 3782	1 6818		5 1915	5 4889
18		6704 70		1 3631	1 6954		5 3185	5 6448
19		7042 39		1 3492	1 7140		5 4539	5 8129
20		7366 37		1 3362	1 7382		5 6005	5 9969
21		7673 99		1 3241	1 7687		5 7628	6 2018
22		7961 95		1 3132	1 8056		5 9475	6 4346
23		8226 14		1 3032	1 8486		6 1648	6 7049
24		8461 71		1.2946	1 8958		6 4309	7 0271
25		8663 19		1 2873	1 9431		6 7728	7 4237
26		8824 95		1 2815	1 9802		7 2402	7 9341

(a) Vidal and Stwalley [15], (b) Al-Tuwirqi *et al* [12] and (c) Sharma *et al* [13]

used these coefficients in the computer programme of Le Roy [7] and calculated the r_{max} and r_{min} of each vibrational level of the $A^1\Sigma^+$ state of ^{7}LiH (Table 2).

Sharma *et al* [13] in their comment point out that they use the same Dunham coefficients as used by Al-Tuwirqi *et al* [12] and find that around $v' = 14$ the value of r_{min} starts to increase. They remark that this unphysical situation has not been found by Al-Tuwirqi *et al* [12] and it opens questions for their potential energy curve.

We have looked into this comment of Sharma *et al* [13]. As said above, the anomalous behaviour of the A state is common to all the alkali hydrides and its Dunham coefficients $Y_{20}(\approx -w_e x_e)$ and $Y_{11}(\approx -\alpha_e)$ have positive signs (Stwalley *et al* [14]). Sharma *et al* [13] used the same Dunham coefficients as used by Al-Tuwirqi *et al* [12]. We find that they have used the negative sign of Y_{11} when it is given positive sign in Table (3) of Ref. [10]. Al-tuwirqi *et al* [12] calculated the potential energy curves with signs of Y_{20} and Y_{11} as positive. It is this wrong sign of Y_{20} which has given Sharma *et al* [13] the unusual behaviour of the $A^1\Sigma^+$ state of ^{7}LiH different from that of Al-Tuwirqi *et al* [12]. It can be seen in Table 2 where the values of r_{min} and r_{max} are compared with the values of Vidal and Stwalley [15] recommended by Stwalley *et al* [16]. It is seen that Al-Tuwirqi *et al* [12] give values of the potential curve close to those of Vidal and Stwalley [15] whereas the values of Sharma *et al* [13] do not agree with them. The difference of these values are quite pronounced when the potential curves are plotted from the values of Al-Tuwirqi *et al* and Sharma *et al* (Figure 1). It is added here that our group also constructed the RKR potential curves of the $A^1\Sigma^+$ states of NaH [17] and KH [18] using the Dunham coefficients Y_{20} and Y_{11} with positive signs in their calculations. Their results are found to agree with those recommended by Stwalley *et al* [14]. The method used by us in these calculations has been further supported by Camacho *et al* [19]. Their values of r_{min} and r_{max} of the $A^1\Sigma^+$ state of KH are in perfect agreement with those of our

values [18]. The computer programme of Le Roy [7] used in our calculation of the RKR potential curve is based on the

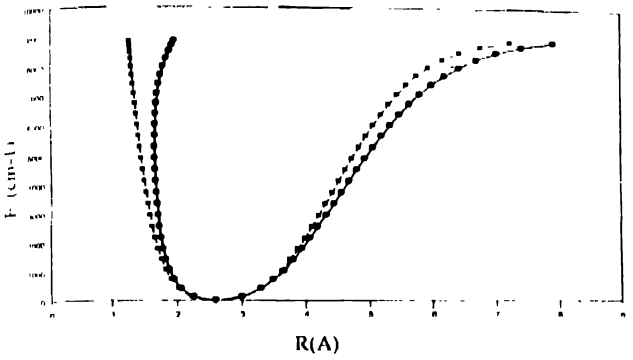

Figure 1. ^{7}LiH A-X system —●— Sharma *et al* ---×--- Al-Tuwirai *et al*

quadrature procedure suggested by Tellinghuisen [6] and includes a number of improvements. The improved ability to give accurate potential curves for the $A^1\Sigma^+$ states of alkali hydrides which show quite anomalous behaviour [11] is an important feature of Le Roy's programme.

To conclude, the unphysical situation found by Sharma *et al* [13] in the RKR potential curve of the $A^1\Sigma^+$ state of ^{7}LiH of Al-Tuwirqi *et al* [12] is due to the use of negative sign of Y_{11} which was actually positive as shown in Table 3 of Ref. [10]. The calculations of Al-Tuwirqi *et al* agree with the recommended values [16] as they have used the positive signs of Y_{11} and Y_{20}. The other details given by Sharma *et al* [13] to present their point of view in this respect need to be reconsidered in the light of the correct signs of the Dunham coefficients used in the potential curve calculations of the $A^1\Sigma^+$ state of ^{7}LiH.

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